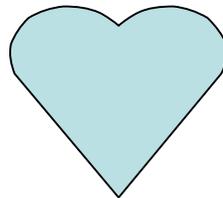


Canonical Phase Diagrams: Honoring the youthful John E. Morral on reaching the venerable age of 65.

John W. Cahn

National Institute of Standards and
Technology, MSEL, Gaithersburg, MD
20899-8555 USA

TMS, San Francisco, February 14, 2005



Morallisms, ca. 1967

Do we have to do things in standard ways?

Why not explore phase diagram axes other than
T or S, P or V, concentration or μ ,
for phase diagrams?

Somewhat later, ca. 1980:

Why not find other ways to report and use diffusion coefficients?

This hen was and still is willing to learn from the egg.

Morallisms in Print

- “On Characterizing Stability Limits for Ternary Systems,” *Acta Metall*, 1972, 20, 1061.
 - Stab. Lims. for Ternary Regular Systems, *ibid.* p. 1069.
- “Two-dimensional phase fraction charts,” *Scripta Metall*, 1984, 18, 407.
- “Constructing multicomponent phase-diagrams by overlapping ZPF lines,” *Scripta Metall*, 1986, 20, 889.
- “Phase-boundary, ZPF, and topological lines on phase diagrams,” *Scripta M&M*, 1991, 21, 1993.
- “2-Dimensional sections of miscibility gaps-The rose geometry,” *J. CHIM PHYS ET PHYS-CHIM BIOLOGIQUE*, 1993, 90, 421.
- “The square-root diffusivity,” *Acta Metal*, 1986, 34, 2201
- “Zigzag diffusion paths in multiphase diffusion couples,” *Acta M&M* 1994, 42, 3887

“On Characterizing Stability Limits for Ternary Systems”

JEM, Acta Metall, 1972, 20, 1061 (and 1069)

The molar free energy of a solution F and its various derivatives with respect to concentrations can be used instead of the concentrations as the axes of phase diagrams. Such axes were explored by John Morral in this paper. **He found that when phase diagrams are plotted with second derivatives* of F as axes instead of with the usual temperature and concentration axes, all regular solutions phase diagrams are distorted into triangular pyramids on a **universal canonical phase diagram, in which stability limits are depicted as a double cone.**** The cones marks the stability limit with respect to spinodal decomposition. A solution's regular solution interaction parameters determines placement of each triangular pyramid phase diagram with respect to the double cone.

*Second derivs of F are related to the thermodynamic factor in D .

Canonical Stability Limits mapped onto a Ternary Phase Diagram

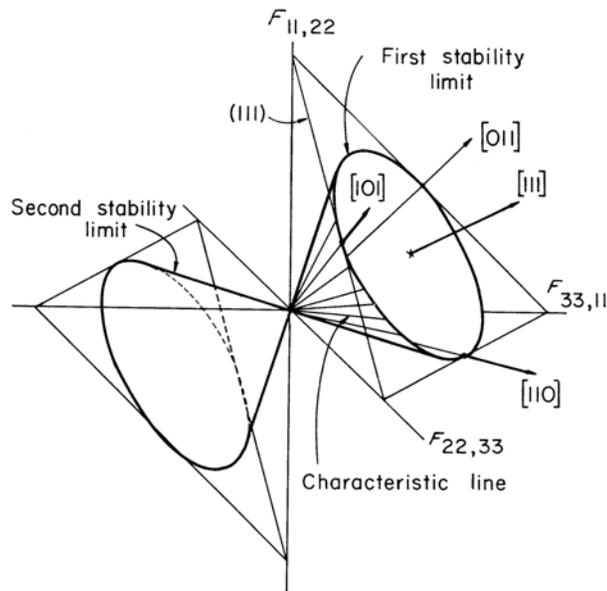
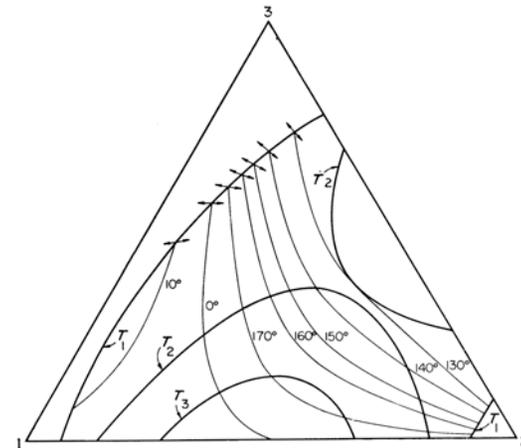
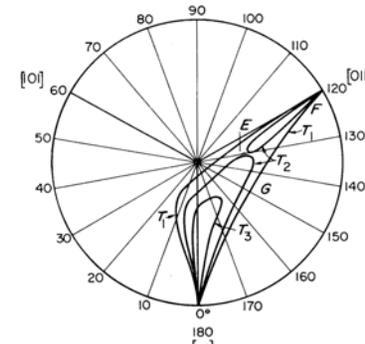


FIG. 2. The stability limit and the characteristic lines plotted as a double cone in a space defined by three $F_{ii,jj}$ derivatives.



(a)



(b)

FIG. 4. Example two: the isothermal contours and characteristic lines for a system with two unstable binaries.

The Hen's Canonical Phase Diagrams

ABSTRACT This talk will explore two other choices of thermodynamic functions as axes.

Phase diagram plots using axes of chemical potentials instead of concentration, as suggested by Scatchard and later by Pelton, are useful, more so if carried further

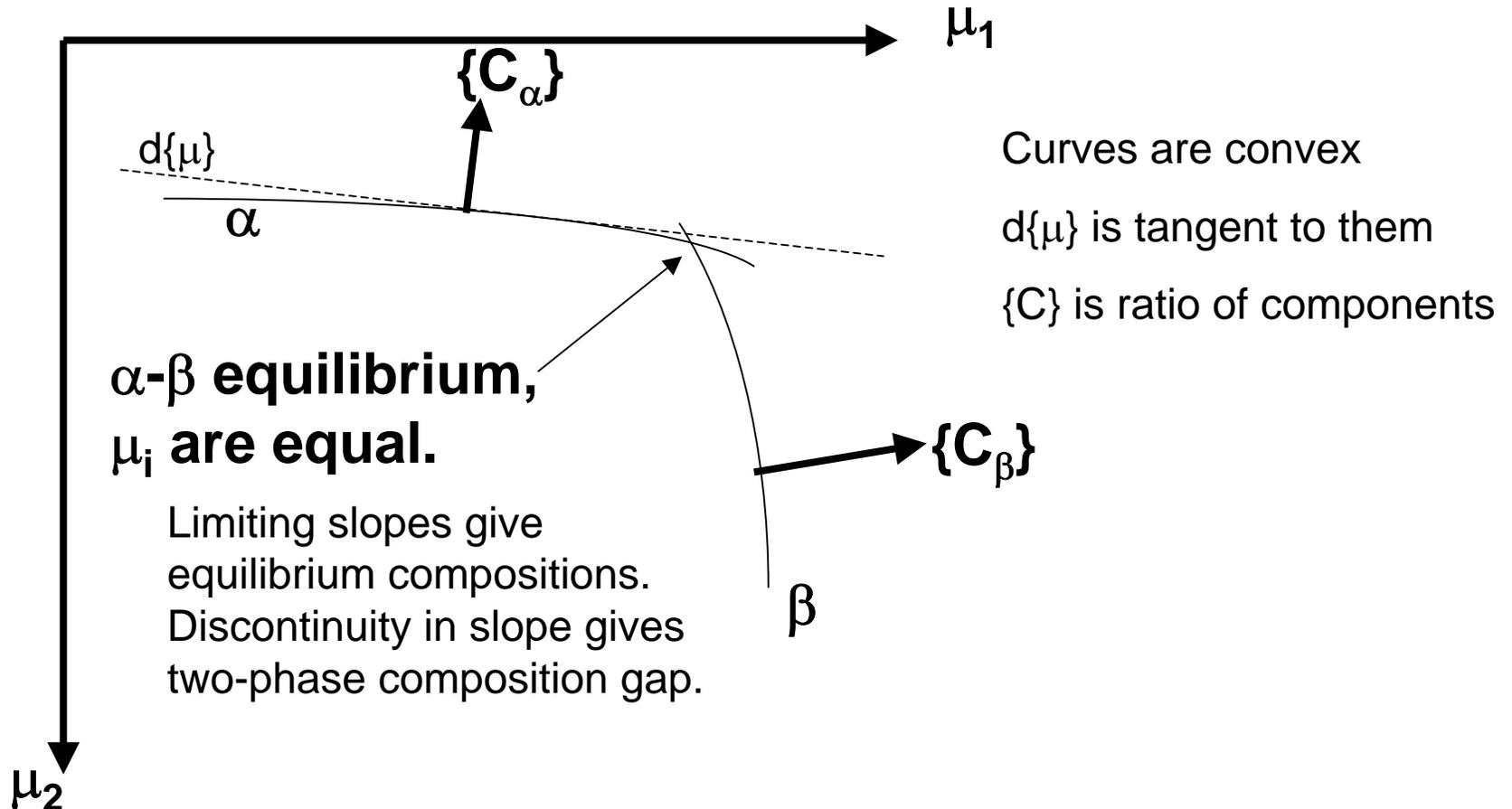
Using derivatives of F with respect to concentration (Morral) and order parameters (Landau) as axes gives canonical phase diagrams and insight into complex ordering, such as for Cu-Au, involving first-order phase transitions and more than one ordered phase.

Scatchard Plots

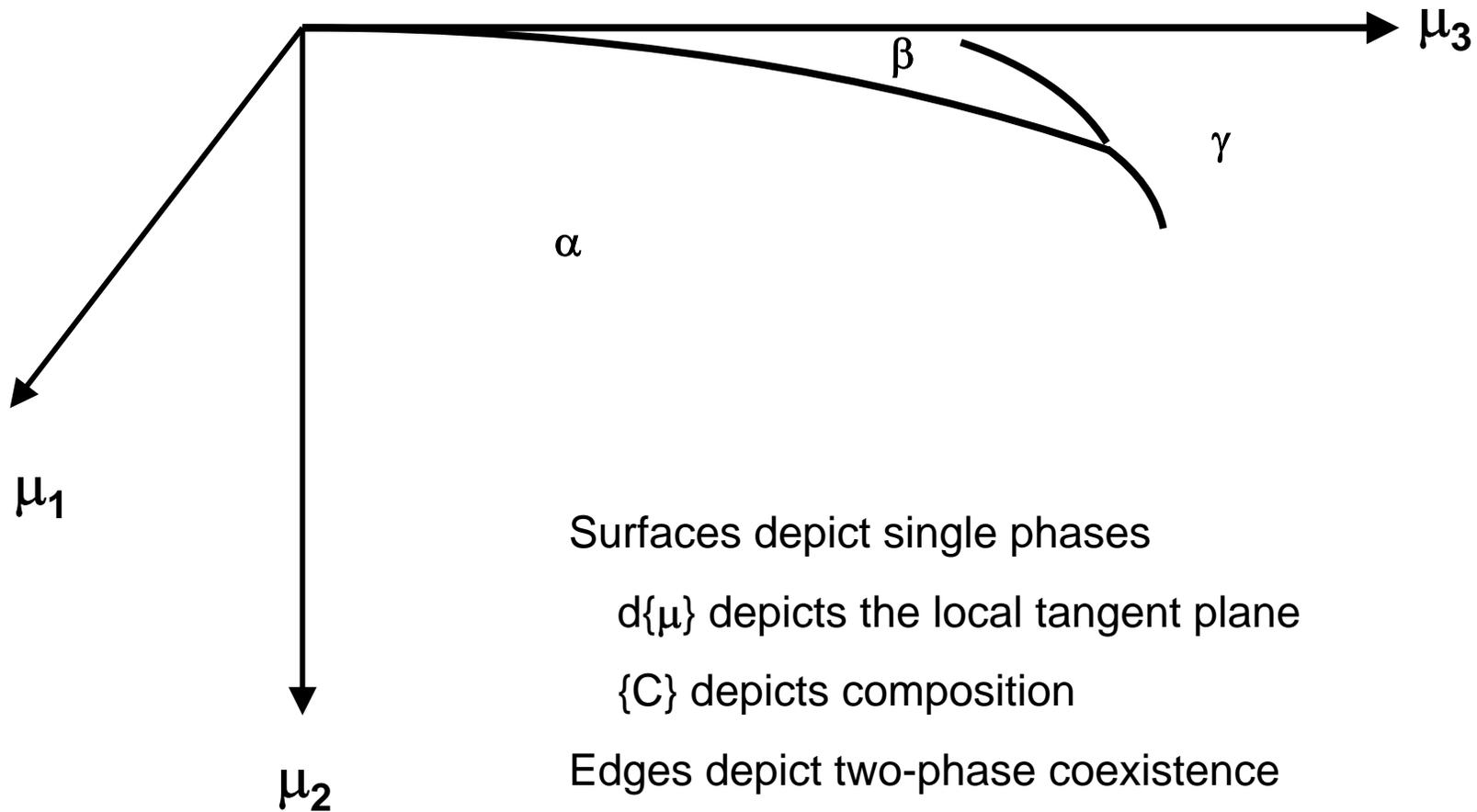
G.Scatchard, The calculation of compositions of phases in equilibrium, JChS, 1940, 62, 2426.

- Let every one of the chemical potentials μ_i be an axis of an isothermal plot.
- Data for μ for the N components give a N-1 dimensional surface in a N-dimensional diagram.
- The tangent to this surface is $d\{\mu\}$. We can think of a $\{\mu\}$ vector.
- By the isothermal Gibbs-Duhem equation,
- $\sum_i C_i d\mu_i = 0$; or $\{C\}.d\{\mu\} = 0$,
- the components of the normal to this surface $\{C\}$ is the composition.
- Phase equilibria are corners, edges, etc. on such plots.

An isothermal binary solution example of a Scatchard Plot.



An isothermal example of a Scatchard Plot for a ternary.



Surfaces depict single phases

$d\{\mu\}$ depicts the local tangent plane

$\{C\}$ depicts composition

Edges depict two-phase coexistence

Corners depict three-phase coexistence

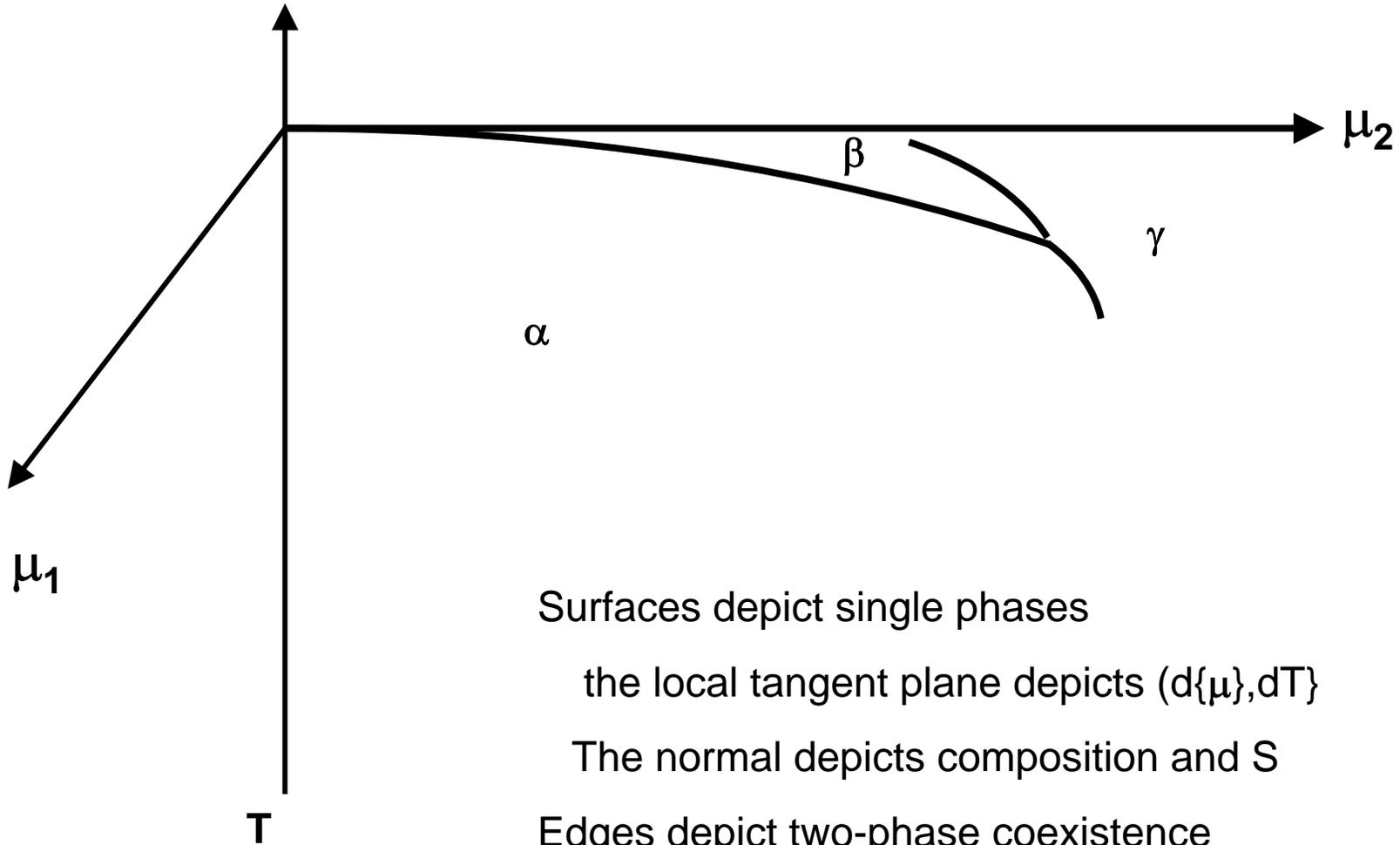
Scatchard Plot data issues

- Need μ for every species
 - Some can be gotten directly from EMF, vapor pressure, etc.
 - Knowing the concentration and using the Gibbs-Duhem equation gives us an independent estimate of the $d\mu_i$.
 - Or an opportunity for interpolating and extrapolating missing data
 - Which is the basis of the Gibbs-Duhem integration for getting other μ from a measured μ (Darken), and closely related to the Wulff construction for crystal shapes (Cahn & Carter).
 - Some μ can be gotten by differentiating F_M , but how accurately do we know F_M ?
- Finding edges and corners and limiting slopes is surely more accurate than finding common tangents to and make better use of the data used to determine F_M .
- Opportunities:
 - There are excellent methods for interpolation and extension whenever data are missing.
 - Ideas for methods for CALPHAD & para-equilibrium?

A generalization of Scatchard Plots.

- Gibbs-Duhem Eqn.
- $\sum_i N_i d\mu_i + SdT - VdP = 0$
- Let axes of the plot be T , P (but only if pressure is varied), and the μ_i .
- Data for the system form hypersurfaces, $f_\alpha(\mu_i, T, P) = 0$; a vector (μ_i, T, P) .
- The normal to these surfaces gives ratios of the concentrations of the components, S , and V .
- Intersections (edges, corners, etc.) give equilibria among phases, and the limiting normals give not only the compositions, but also the entropies and volumes of the co-existing phases, and, of course, composition jumps, ΔS and ΔV .

An example of a Scatchard Plot for a binary with T (at P const).



Surfaces depict single phases

the local tangent plane depicts $(d\{\mu\}, dT)$

The normal depicts composition and S

Edges depict two-phase coexistence

Corners depict three-phase coexistence

CALPHAD & Scatchard compared when sketchy phase diagram data are all we have.

- Scatchard
 - The compositions of each phase in an equilibrium give the slopes of edges and phase surfaces. How to connect them?
- CALPHAD

Too bad that Morral was an infant in 1940.

Both John and F,R. Morral had chances to meet Scatchard.

Scatchard remained active after his retirement and was a great help to us with the experimental techniques and data handling for Ron Heady's thesis.

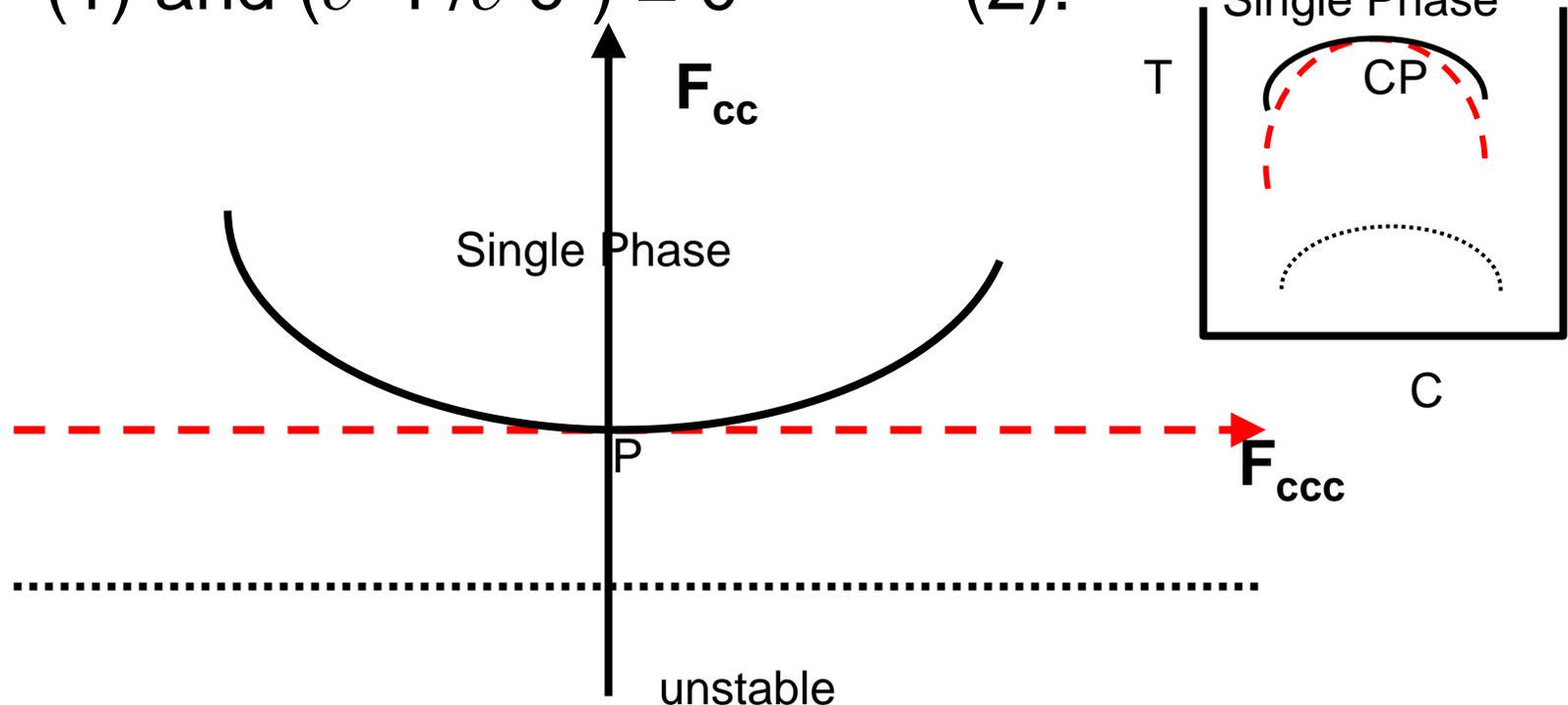
Canonical phase diagrams using higher derivatives of F

- Ternary example: Morall's paper.
- Simpler examples:
- Critical point and spinodal in a binary.
- Ordering
- Series expansion of F in terms of composition c and order parameter η about a critical point.
 - $F - F_{\text{crit}} = \sum_{nm} (1/n!m!) (\partial^{n+m} F / \partial \mathbf{c}^n \partial T^m)_c (\mathbf{c} - \mathbf{c}_{\text{crit}})^n (T - T_{\text{crit}})^m$
- **Then let the $(\partial^{n+m} F / \partial \mathbf{c}^n \partial T^m)_c$ be the axes.**

Unmixing near a critical point:

A simple classical binary example

- Chem spinodal ----- $(\partial^2 F/\partial c^2) = 0$ (1),
 - Coherent spinodal $(\partial^2 F/\partial c^2) + 2 Y\eta^2 = 0$
- Conditions for a chemical critical point, CP
 - (1) and $(\partial^3 F/\partial c^3) = 0$ (2).

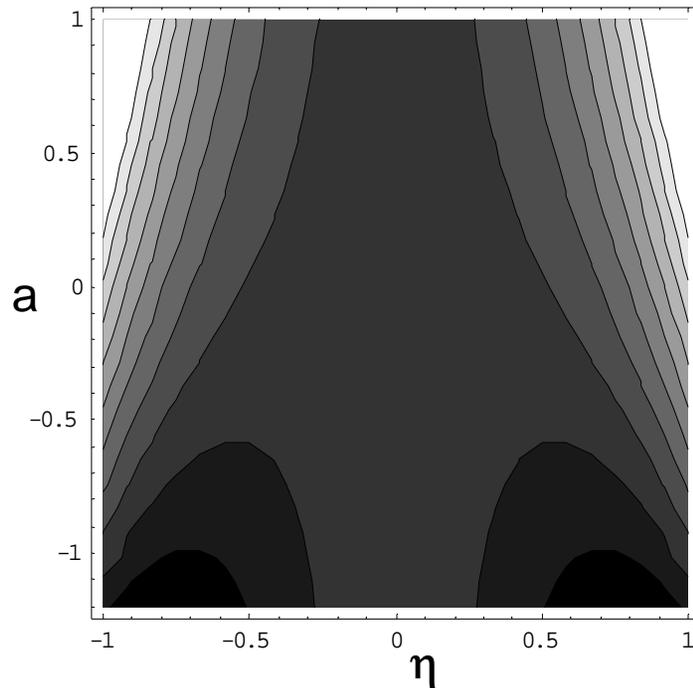


Given F_{cc} and F_{ccc} ; can we solve for c and T uniquely?

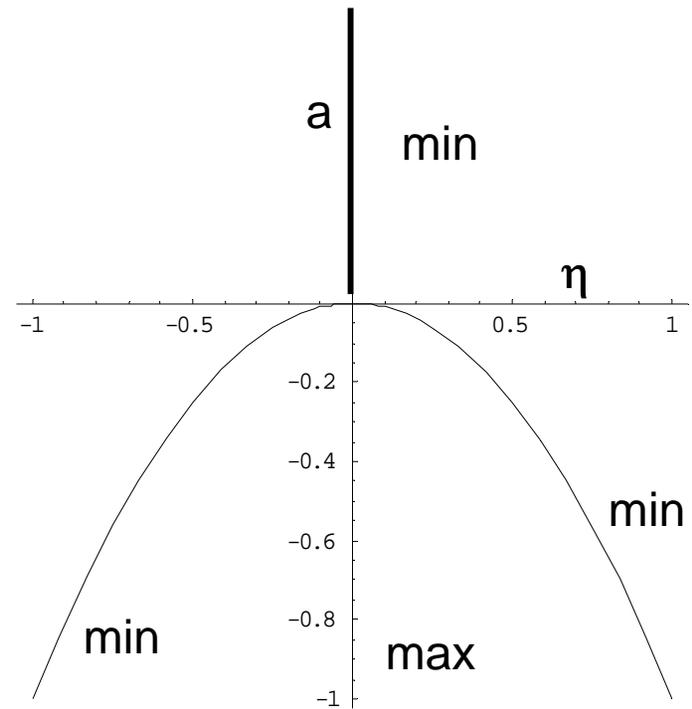
- Almost always; away from $T=0$ and $c=0$ or 1 .
- Example: Let $F/RT = (\Omega/RT) c(1-c) - \{c \log c - (1-c) \log (1-c)\}$.
- $F_{cc} = -2 \Omega/RT - 1/[c(1-c)] = 0$
- $F_{ccc} = \{1-2c\}/[c(1-c)]^2 = 0$
- Solutions:
- For critical point; $c = 1/2$; $\Omega/RT = -2$
- For coexistence near T_c ; $F_{ccc} = F_{cc}^2$

$$F - F_c = a_2(T, c)\eta^2 + a_4\eta^4$$
$$a_4 > 0$$

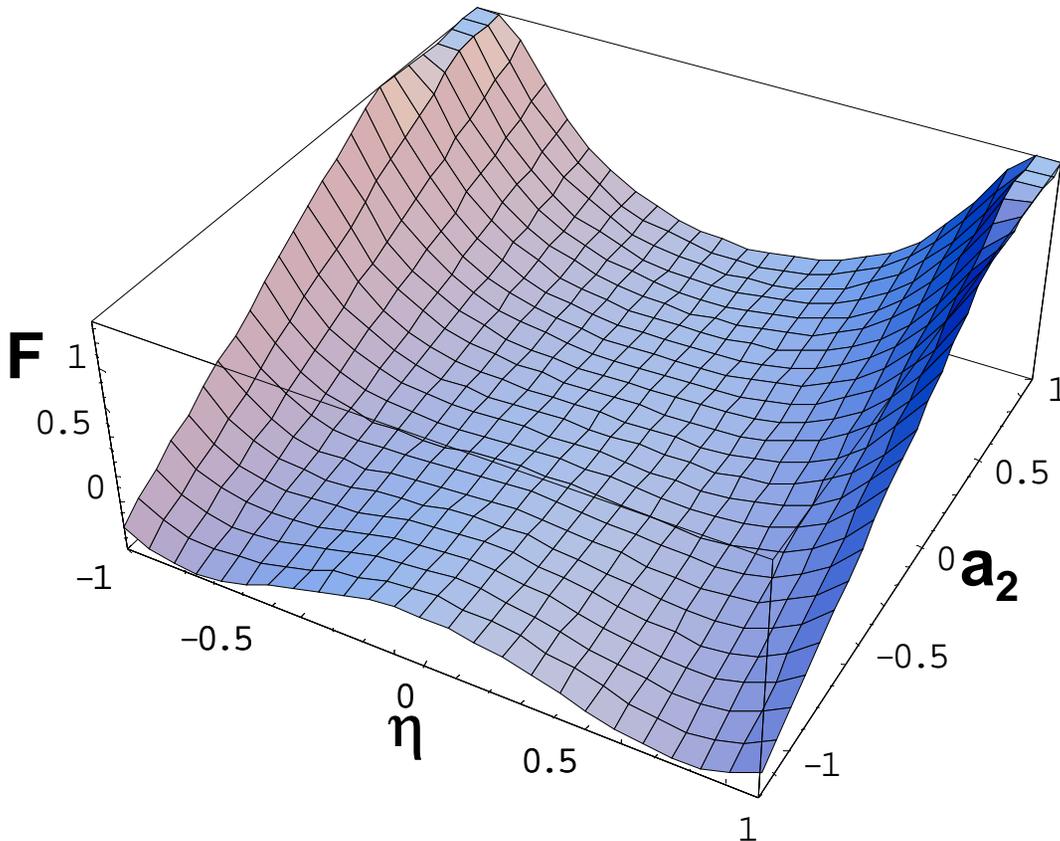
contour



extrema



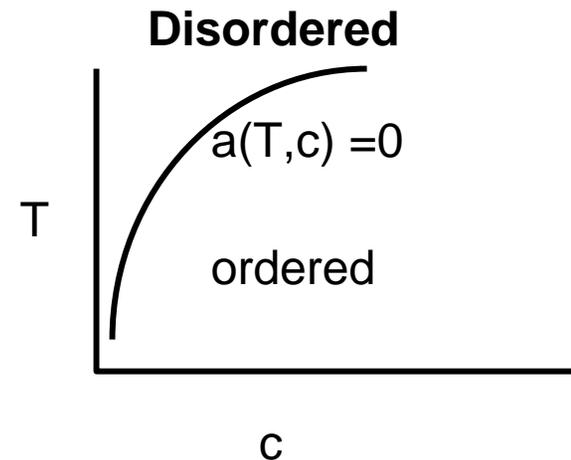
Plot of $F - F_c = a_2(T, c)\eta^2 + a_4\eta^4$



Disordered ($\eta = 0$)

if $a > 0$

Order-disorder line on
phase diagram is
 $a(T, c) = 0$



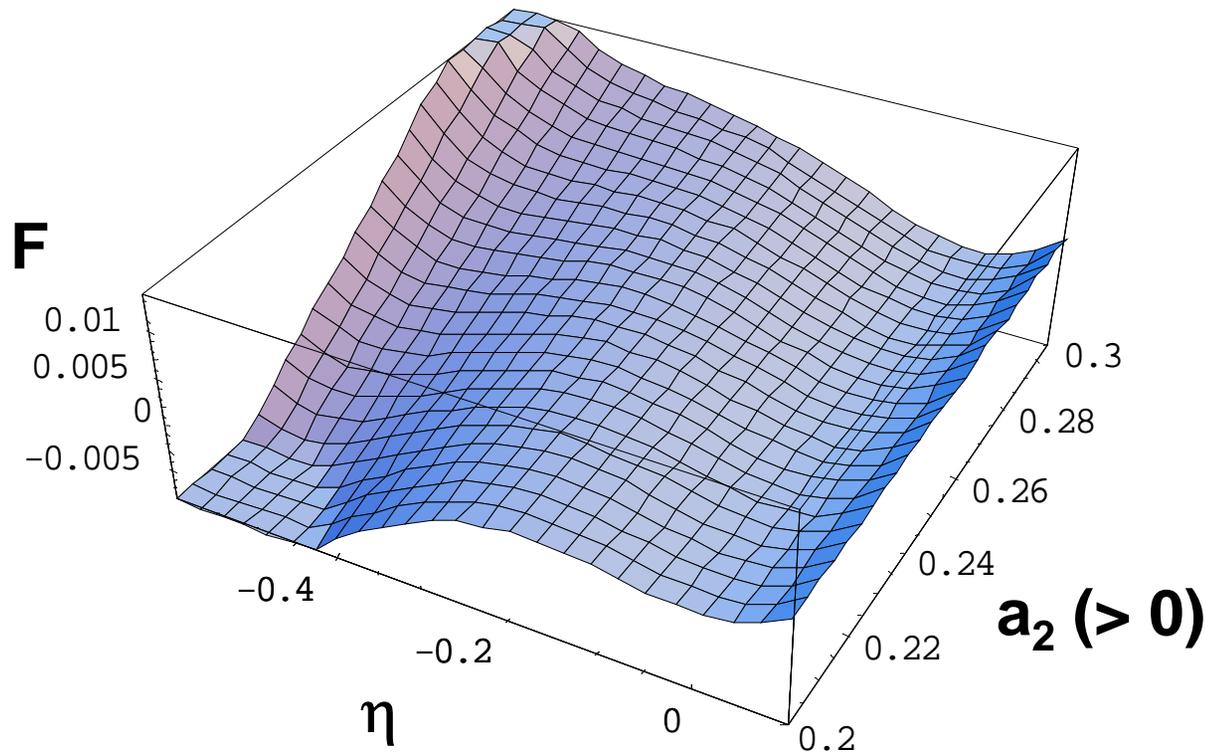
$$\text{Additions to } F - F_c = a_2(T,c)\eta^2 + a_4\eta^4$$

with $a_4 > 0$

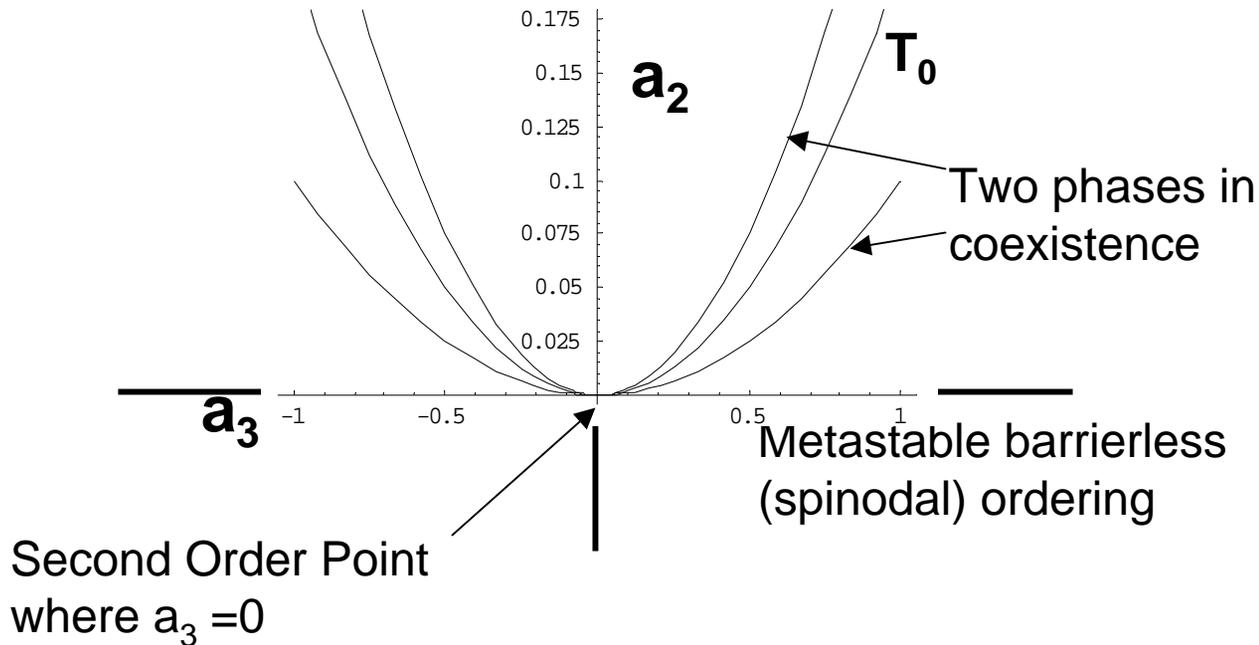
- Linear: $F - F_c = a_1\eta + a_2\eta^2 + a_4\eta^4$
 - Eliminates (smears out) transition
- Cubic: $F - F_c = a_2(T,c)\eta^2 + a_3(T,c)\eta^3 + a_4\eta^4$
 - First order transition, except where $a_3 = 0$
- Higher order: Nothing changes, if $a_4 > 0$
- Negative a_4 . Higher even order, e.g. $a_6 > 0$:
 $F - F_c = a_2(T,c)\eta^2 + a_4\eta^4 + a_6\eta^6$
 - Eliminates second order transition.

Adding a cubic term

Curve ($a_2 = f(a_3)$) for which $\Delta F = 0$ is transition in a single component system; it is the T_0 in a binary or higher order system.



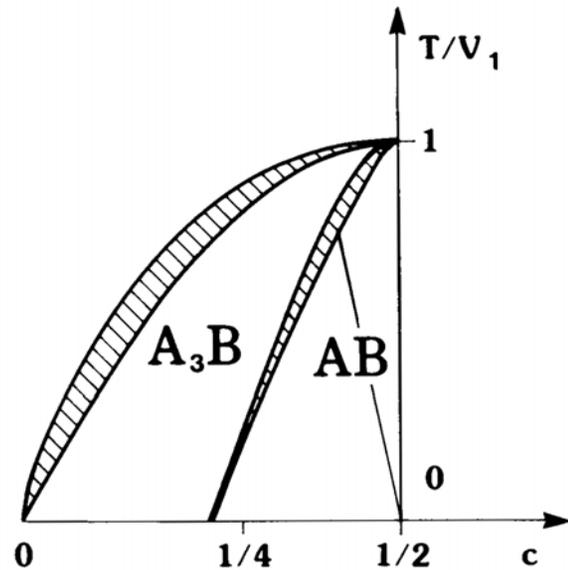
Canonical phase diagram with a cubic term



Corresponding phase diagram with a cubic term has a second order transition at a single critical point, first computed by Shockley.

This point is submerged (metastable) by a first-order congruent o-d transition when $a_4 < 0$.

Multiphase critical point

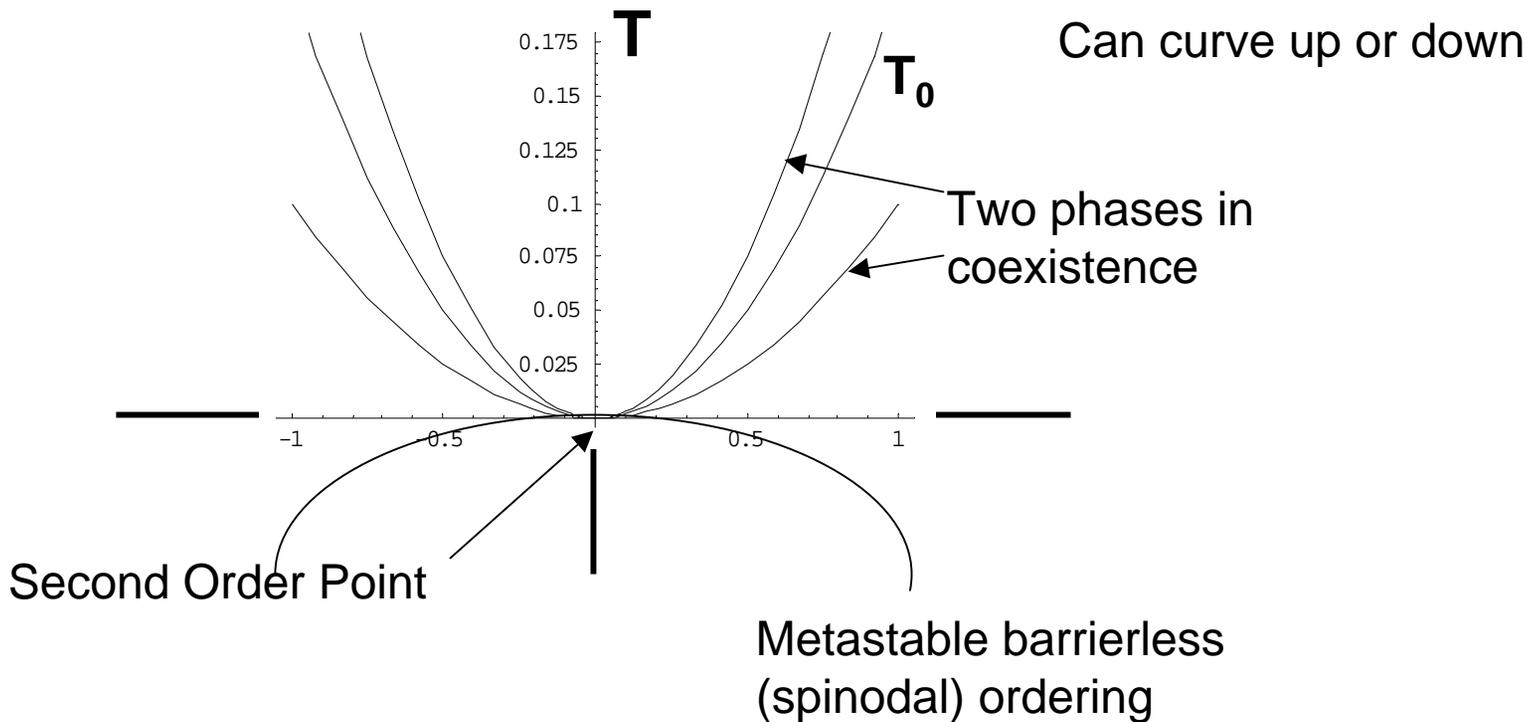


All four phases, disordered fcc, A_3B , AB , and AB_3 , become identical.

All latent heats and interfacial surface energies $\rightarrow 0$.

Fig. 5.32. Schematic mean field phase diagram for the fcc Ising model with nearest-neighbour interactions. After Shockley (1938) and Gahn (1973, 1974). The line within the AB domain separates the high-temperature $L1_0$ phase from the low-temperature L' phase (see sect. 4.4.1).

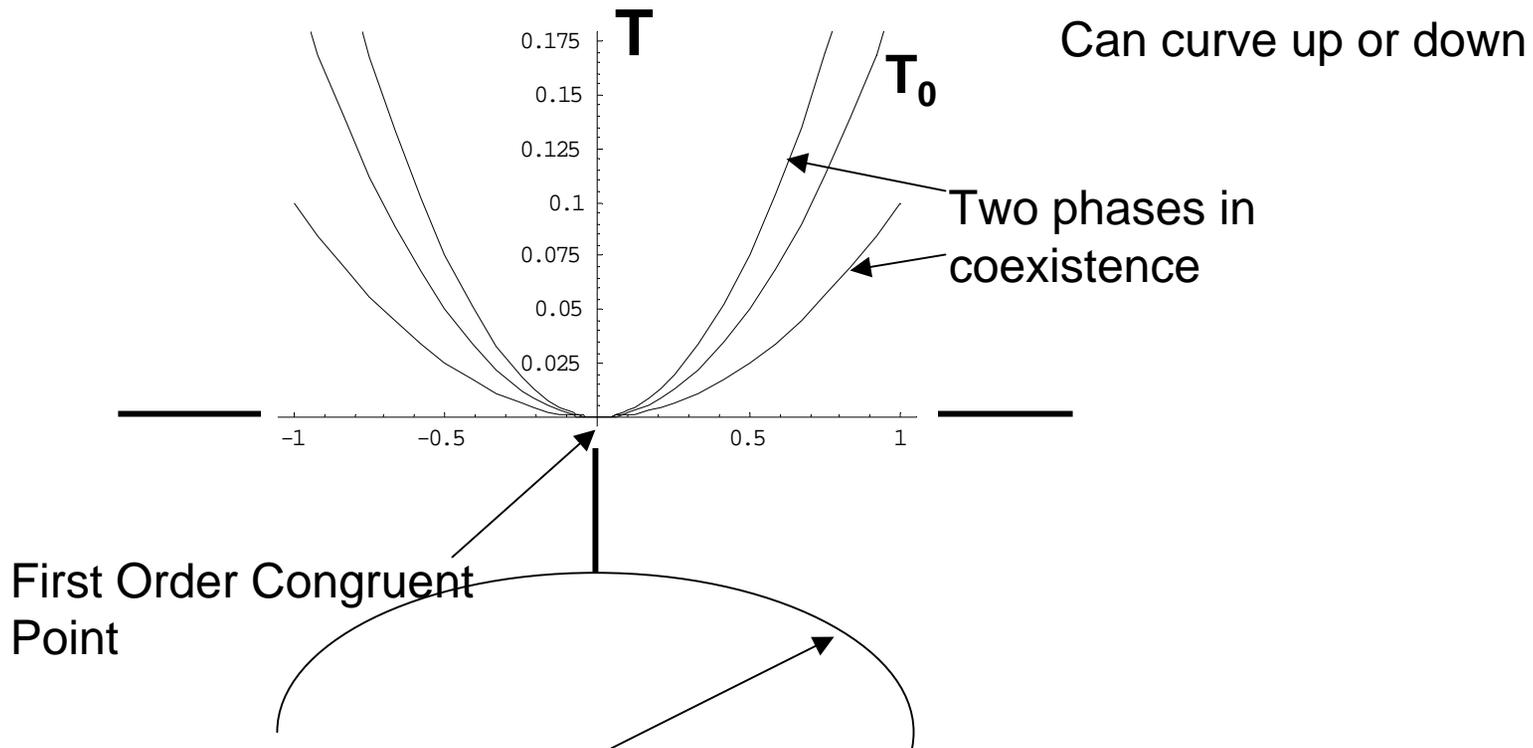
Phase diagram with a cubic term



Corresponding phase diagram with a cubic term has a second order transition at a single critical point, first computed by Shockley.

This point is submerged (metastable) by a first-order congruent o-d transition when $a_4 < 0$.

Phase diagram with a cubic term and with $a_4 < 0$



Metastable barrierless (spinodal) ordering is submerged (metastable) by a first-order congruent o-d transition when $a_4 < 0$.

CVM Phase diagram

Latent heat $\rightarrow 0$

$\Delta c \rightarrow 0$

IPB $\sigma \rightarrow 0$

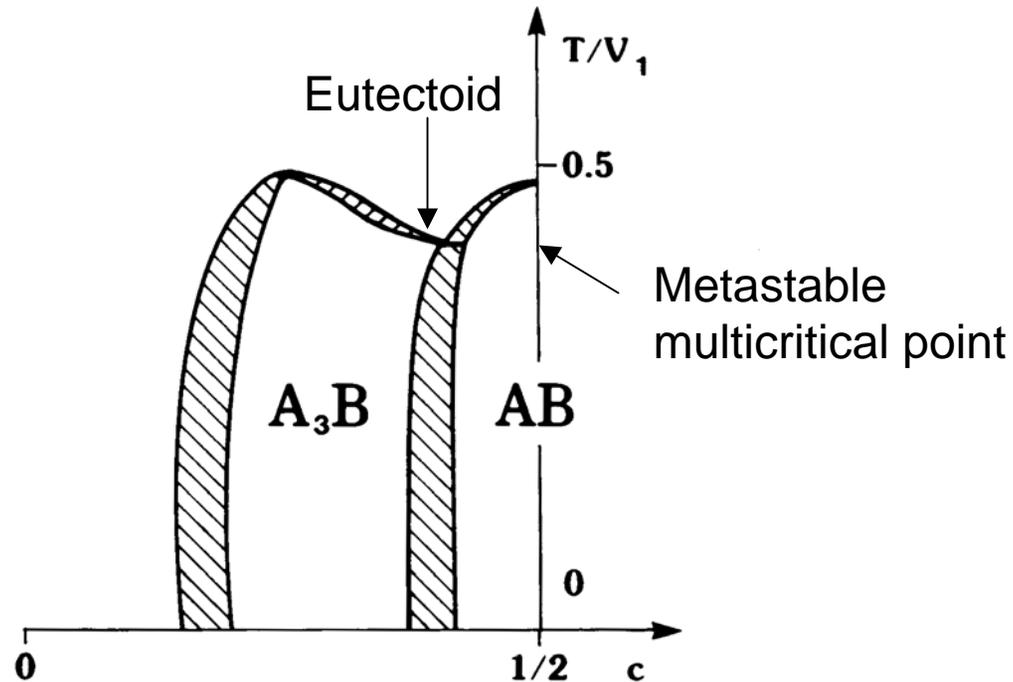


Fig. 5.34. Schematic CVM phase diagram within the tetrahedron approximation. After Van Baal (1973) and Kikuchi (1974).

At metastable crit point, σ , the energy of the interphase interface $\rightarrow 0$

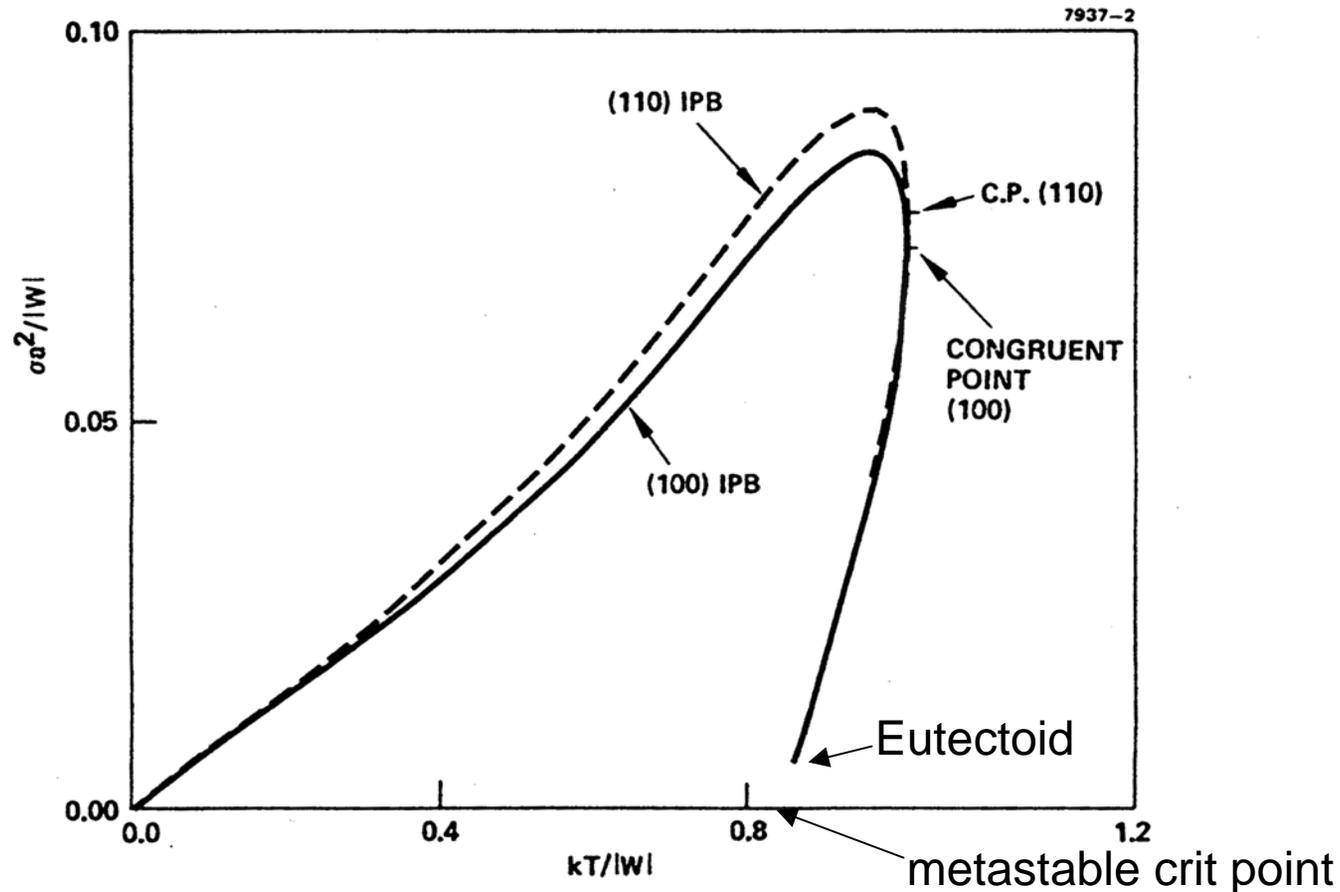
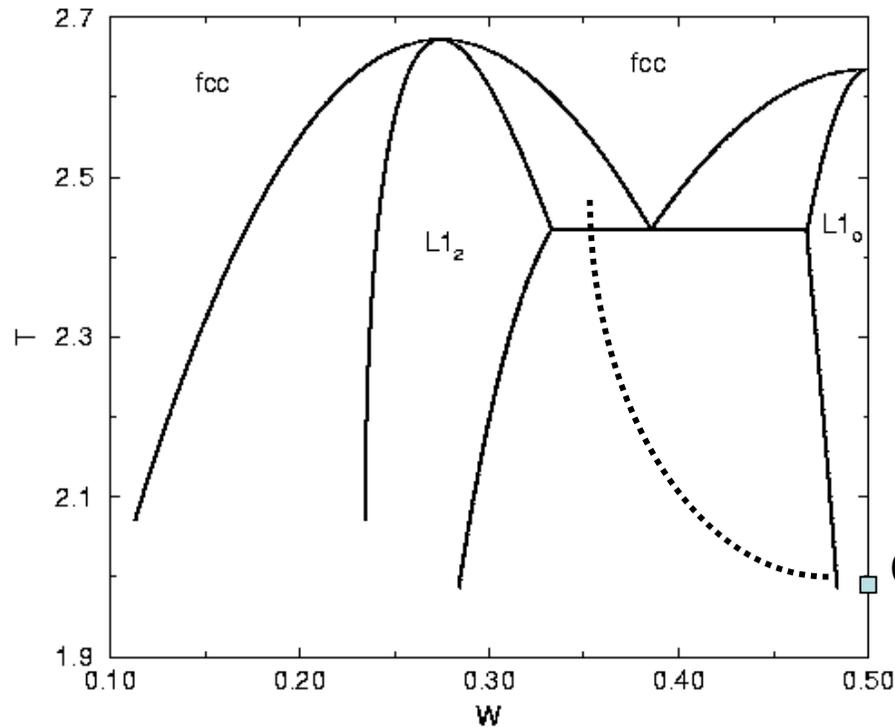
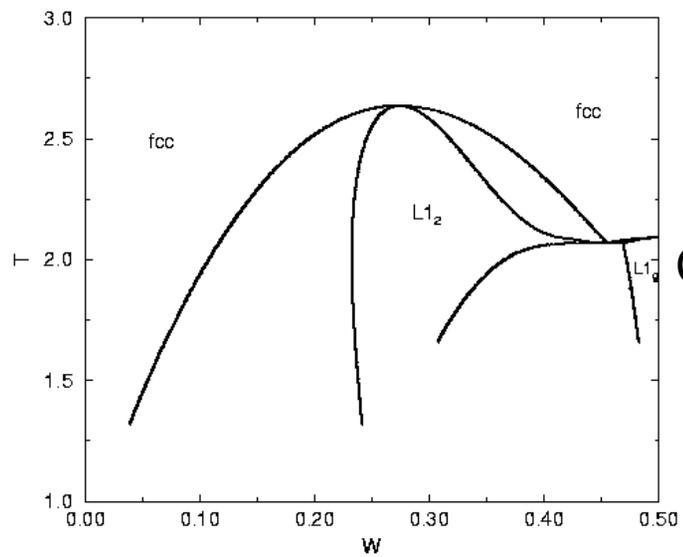


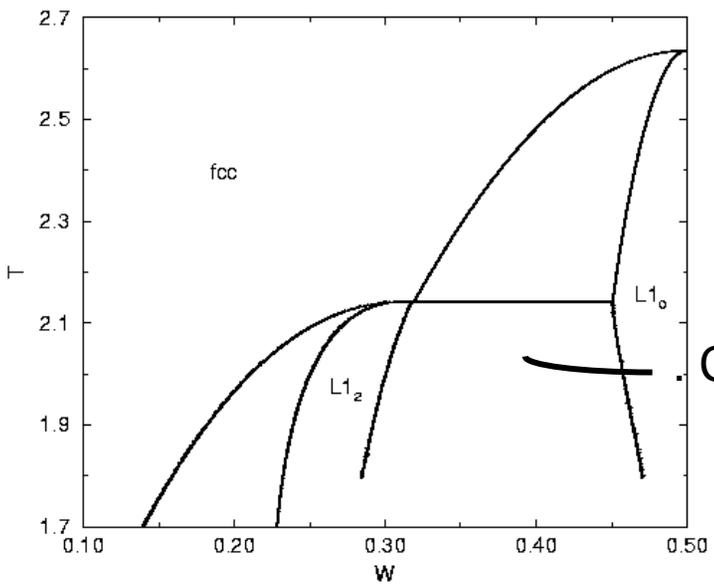
Fig. 7. The reduced free energy σ of the interphase boundary between f.c.c. and the $L1_2$ structure as a function of reduced temperature for (100) and (110). The peak in σ does not occur at the peak temperature.

R.J. Braun, J. Zhang, J.W. Cahn, G.B. McFadden, and A.A. Wheeler, Model phase diagrams for an FCC alloy





Crit. pt



Crit. pt

Summary

- Not doing things in standard ways has been a big part of John Morral's life. He has shown it is fun, instructive, and can give valuable new insights.
- In this talk I re-examined two non-standard ways of plotting phase equilibrium data, Scatchard's and Morral's. Both used as axes derivatives of free energies.
- Are Scatchard and Morral kindred souls? Scatchard 1940 plots are based on profound insights, but were not adopted. Ditto for the 1962 Morral plots. Are they worth resurrecting after 65 years?
- There may be some data handling advantages in this age of computers and sparse, often inaccurate data.
- Some are canonical and reveal general principles, e.g. the multiphase critical point in FCC.

Last slide

Corresponding phase diagram with cubic term

Bo Sundman, Suzana G. Fries and W. Alan Oates, A CALPHAD
Assessment of the AU-Cu System using the Cluster Variation
Method, Zeitschrift Metallkunde 90 (1999) 267-273.